COPPER REMOVAL FROM AQUEOUS SOLUTION USING AMBERLITE IR-120 CATION EXCHANGER MIXED MATRIX MEMBRANE CHROMATOGRAPHY

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ABSTRACT

Copper is one of the toxic heavy metals that contaminated in industrial wastewater. Cation exchange chromatography is widely used for the removal of copper (II)from the water. In this study, Amberlite IR-120 cation exchanger resin was used to prepare mixed matrix membrane (MMM) chromatography by blending the resin in ethylene vinyl alcohol (EVAL) base polymer solution. The EVAL composition was varied in the range of 15to 20 wt% with fixed Amberlite IR-120 loading at 30%. The adsorption isotherm of cation MMM was determined from batch binding experiment. From the result, it shows that MMM15,prepared at 15 wt% EVAL gave high amount of copper binding of 5688.190 mg Cu/g adsorbent.In regeneration experiments using 0.1M HCl, more effective regeneration was showed byMMM20, prepared at 20 wt% EVAL, than EVAL membrane.

PENYINGKIRAN TEMBAGA DARI LARUTAN AKUEUS MENGGUNAKAN AMBERLITE IR-120 PENUKAR KATION CAMPURAN MATRIX MEMBRAN KROMATOGRAFI

ABSTRAK

Tembaga adalah salah satu logam toksik berat yang tercemar dalam air sisa industri. Kromatografi pertukaran kation digunakan secara meluas untuk penyingkiran kuprum (II) dari air. Dalam kajian ini, Amberlite IR-120 resin penukar kation telah digunakan untuk menyediakan matriks membrane campuran (MMM) kromatografi dengan menggabungkan resin dalam etilena vinilalkohol (EVAL) polimer asas penyelesaian. Komposisi EVAL telah diubah dalam julat antara 15 hingga 20% berat dengan tetap Amberlite IR-120 loading 30%. Isoterma penjerapan kation MMM telah ditentukan dari eksperimen kelompok mengikat. Dari hasilnya, ia menunjukkan bahawa MMM15, disediakan pada 15% berat EVAL memberikan jumlah yang tinggi tembaga mengikat 5688,190 mg Cu / g adsorben. Dalam eksperimen semula menggunakan 0.1M HCl, lebih regenerasi berkesan telah menunjukkan oleh MMM20, disediakan di 20 wt% EVAL, daripada membran EVAL.

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LIST OF SYMBOLS

°C	Degree celcius
g	Grams
L	Litre
mL	Millilitre
s	Seconds
w/w	Weight per weight
%	Percentage
q	Dynamic binding capacity
V	Volume
C_o	Initial concentration
C_f	Equilibrium Cu concentration
m	Mass
R	Percentage of resin loading
W_r	Amount of resin
W_p	Amount of EVAL
A	Area
t	Operation time

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
Cu	Copper
Cr	Chromium
DMSO	Dimethyl Sulfoxide
EVAL	Ethylene vinyl alcohol
HCl	Hydrochloride acid
MMM	Mixed Matrix Membrane
Ni	Nickel
ppm	Parts per million
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Industrial wastewater is one of the serious environmental problems in the natural eco-system because the wastewater contaminated with heavy metal due to the improper wastewater treatment. Heavy metals pollution occurs in a lot of industrial wastewater. For example the industrial wastewater produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries (Abdel Salam *et al.*, 2011). This industrial wastewater usually contains Cu, Pb, Zn, Cd, Ni, and Cr (Argun *et al.*, 2008). When the toxic heavy metals are bare to the natural eco-system, accumulation of metal ions in human bodies will occur through either food chains or direct intake. Hence, to solve this problem, heavy metals must be prevented from reaching the natural environment (Meena *et al.*, 2008).

Copper (II) is one of the toxic heavy metal. There are a lot of industrial that use of copper to produce product, due to its features like malleability, resistance to corrosion, high conductivity and thermal conductivity. Copper is alloyed with nickel and used in form of cupronickel for shipbuilding. This is due to in this form it is highly resistant to corrosion. Besides, copper in liquid form is used as a wood preservative which can helps in restoration of original structures that are damaged due to dry root. Unfortunately, high dose of copper can cause liver impaired, kidney failure, gastrointestinal disturbance and others health problem (Futlan *et al.*, 2011). Maximum contaminant level of copper is 1.3mg/L according to US Environmental Protection Agency (Ghassabzadeh *et al*., 2010).

Several conventional methods have been used in order to remove toxic heavy metals from wastewater, such as chemical precipitation, coagulation, solvent extraction and filtration, evaporation, ion exchange and membrane methods (Panayotova *et al.*, 2003). Adsorption is one of the generally economical and effective processes to remove heavy metal (Li *et al.*, 2012). Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of solid or a liquid, forming a molecular or atomic film. Ion exchange resins have been developed as a main alternative for treating wastewater over the past few decades (Muraview *et al.*, 2000). Ion exchange process was defined as ion is removed out of an aqueous solution and is replaced by another ionic species (Neumann *et al.*, 2009). Selective resins will reduce the residual concentration of heavy metal to below maximum limits (Rauf *et al.*, 2000). Numerous studies on the adsorption of metal ions on ion exchange resins such as Duolite GT-73 (Shaha *et al.*, 2000), NKA-9 (Xingcun *et al.*, 1997), and Dowex A-1 (Mathur *et al.*, 1985) have been reported. In this study, Amberlite IR-120 mixed matrix membrane chromatography is used as the absorbent to remove copper from aqueous solution.

1.2 Problem Statement

Heavy metals can be found in various concentrations in any natural source of water, however the major treatment problems exist in the process water in the industries such as metal mining and smelting operations, foundries, metal planting and finishing, and metal fabricating plants. Heavy metals such as copper, lead and mercury are micro-pollutants and of special interest as they have both health and environmental significance due to their persistence, high toxicity and bio-accumulation characteristics. These can accumulate in living tissue, also causing various disease and disorder.

Copper is one of the heavy metals that can be found in various sources of wastewater such as electronics plating, wire drawing, copper polishing and paint manufacturing. Copper is an important trace element to human being, however, high dose of copper can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Therefore, study need to be conducted in order to find method to reduce the impact of heavy metal contamination in the industrial effluent which can contribute to major water pollution.

In order to remove heavy metal from wastewater, some methods have been suggested such as chemical precipitation, coagulation, solvent extraction, filtration, and evaporation. However, most of the methods have some limitations such as requirement of several pre-treatment as well as additional treatments. Besides, some of the methods are less effective and require high capital cost (Kam *et al.*, 2002; Kim, 2002; Volesky, 1990). Precipitation followed by coagulation has been widely employed for removal heavy metals from wastewater but this technique typically produces large volumes of sludge consisting small amount of heavy metal (Amarasinghe *et al.*, 2007). Ion exchange is one of the effective methods for removal of heavy metal ions, and its operational and economic advantages for treating electroplating rinse water have been discussed (Weltrowski *et al.*, 1996). Several advantages of ion exchange are very compact facility, easy recovery of metals, more versatile than the others methods and no secondary pollutant (Lim *et al.*, 2002).

1.3 Research Objective

The objective of this research is to investigate the feasibility of using mixed matrix membrane (MMM) chromatography using Amberlite IR-120 for the removal copper (II) from aqueous solution.

1.4 Scope of Study

In order to achieve the objective of this study, the scope of the study has been determined as followed:

i. To prepare Amberlite IR-120 MMM based membrane at different EVAL composition, between 15 to 20 % and at 30 % Amberlite IR-120 loading.

ii. To determine the adsorption isotherm of MMM for copper (II) binding.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metal

Heavy metal elements usually exist in different oxidation states, such as soil, water and air. In the water, the ion charges, solubilities and reactivities of this metal are vary widely. For their short term or long term toxic effect, the maximum permissible concentration of this heavy metal in drinking water stated in municipal and industrial discharged are closely regulated through the legislation. There are several example of heavy metal, such as copper, aluminum, magnesium and cadmium. Each of heavy metal elements has their own characteristics. Yan *et al.*, (2003) state that heavy metal present in nature and industrial waste. The presences of heavy metals in surface and groundwater cause a major inorganic contamination problem because of their mobility in natural water and ecosystems and the toxicity. There are different types of heavy metal content for different industries as shown in Table 2.1.

Table 2.1 Example of heavy metal content in effluent samples collected from different industries of Taloja industrial estate of Mumbai
(Source: Lokhande, *et al*., 2011)

Industries	Heavy Metals (mg/L)	Year-1999							Year-2000						
		February	April	June	August	October	December	Average	January	March	May	July	September	November	Average
Engineering	Cr	27.9	31.6	27.2	24.9	27.5	38.7	**29.6**	30.9	34.6	40.2	27.5	20.7	28.5	**30.4**
	Cd	24.9	30.7	25.5	20.4	27.8	26.4	**26.0**	22.7	28.4	34.9	27.5	15.6	17.1	**24.4**
	Ni	14.9	20.1	20.1	10.5	20.1	24.0	**18.3**	19.6	23.6	27.4	24.0	16.2	18.1	**21.5**
	Zn	27.0	31.6	27.1	20.0	24.0	31.4	**26.9**	26.9	29.5	32.1	25.2	20.0	26.2	**26.7**
	Cu	21.6	26.3	26.2	12.9	15.2	23.2	**20.9**	19.1	24.3	32.4	20.1	13.8	19.5	**21.5**
	Pb	21.6	22.8	19.9	11.8	13.2	17.0	**17.7**	19.2	23.0	27.4	20.4	17.1	19.4	**21.1**
	Fe	7.6	8.7	8.0	6.2	6.2	7.1	**7.3**	7.0	9.6	11.5	8.3	6.0	6.8	**8.2**
Paper Mill	Cr	35.0	40.0	30.0	32.5	29.5	45.3	**35.4**	28.3	27.9	39.3	26.9	18.9	26.1	**27.9**
	Cd	21.1	23.2	19	14.5	23.0	19.2	**20.0**	27.3	27.8	31.2	31.9	21.9	25.1	**27.5**
	Ni	15.3	21.4	20.9	11.2	13.2	20.5	**17.1**	21.7	27.2	29.7	24.8	21.2	23.5	**24.7**
	Zn	27.0	32.2	25.6	19.7	21.1	24.7	**25.1**	21.9	37.3	42.6	29.3	23.7	28.2	**30.5**
	Cu	28.2	31.5	29.5	19.7	21.4	30.4	**26.8**	29.2	33.4	37.5	22.8	19.3	27.1	**28.2**
	Pb	17.4	23.2	21.3	14.3	17.3	16.3	**18.3**	23.7	27.2	31.2	23.8	20.3	22.9	**24.9**
	Fe	7.0	7.9	6.9	5.3	6.0	6.4	**6.6**	6.1	7.9	4.9	6.3	5.7	6.4	**6.2**
Fine Chemicals	Cr	22.1	32.1	37.3	29.3	26.3	27.5	**29.1**	29.2	28.3	33.0	19.6	20.1	25.7	**26.0**
	Cd	33.9	41.2	43.2	29.9	26.3	28.9	**33.9**	30.2	25.3	41.4	15.2	29.1	31.7	**28.8**
	Ni	29.7	32.7	31.9	21.8	20.3	27.3	**27.3**	34.2	27.3	37.6	13.3	12.1	25.9	**25.1**
	Zn	28.1	29.8	27.8	20.7	22.2	26.2	**25.8**	31.1	20.4	37.7	18.3	19.7	22.7	**25.0**
	Cu	25.2	29.4	29.9	19.3	21.2	22.7	**24.6**	22.9	24.6	26.1	15.5	18.3	23.1	**21.8**
	Pb	26.0	37.2	36.7	28.5	27.7	28.3	**30.7**	27.4	19.2	35.3	21.4	19.2	24.1	**24.4**
	Fe	7.9	9.9	8.2	6.3	6.9	7.6	**7.8**	7.2	7.9	8.6	7.9	6.1	7.6	**7.6**
Dyes	Cr	14.5	18.2	12.5	9.2	13.2	20.3	**14.7**	17.3	19.5	23.4	18.7	14.7	21.6	**19.2**
	Cd	32.2	37.1	34.3	17.3	29.1	29.4	**29.9**	17.5	18.6	21.3	17.8	10.8	14.3	**16.7**
	Ni	19.4	25.5	21.0	17.6	21.0	25.2	**21.6**	8.4	9.3	12.7	7.7	5.6	7.5	**8.5**
	Zn	39.2	61.3	29.7	21.2	37.3	41.8	**38.4**	17.2	19.2	21.5	14.6	8.3	13.7	**15.8**
	Cu	21.3	17.6	21.0	16.3	19.7	17.5	**18.9**	36.7	61.3	77.0	44.2	31.9	34.9	**47.7**
	Pb	15.2	24.5	20.7	9.3	11.0	14.3	**15.8**	19.7	37.2	46.3	34.8	25.7	29.6	**32.2**
	Fe	5.4	5.4	5.3	4.5	4.1	4.6	**4.9**	7.3	7.9	8.8	7.4	6.0	7.5	**7.5**

2.1.1 Copper

Copper is a reddish metal that occurs naturally in rock, soil, water, sediment, and, at low levels, air. The average concentration of copper in the earth's crust is about 50 parts copper per million parts soil (ppm) or 50 grams of copper per 1,000,000 grams of soil (1.8 ounces or 0.11 pounds of copper per 2,200 pounds of soil). In the periodic table of the elements, copper has its own symbol which is Cu. Copper atomic number is 29, its atomic mass is 63.546, its fusion point is 1,803°C, its boiling point is 2,567°C and it is defined as a non ferrous transition metal. Besides, copper occurs naturally in all plants and animals. Copper is an essential element for all known living organisms including humans and other animals at low levels of intake. At much higher levels of copper, toxic effects can be occurring.

From Agency for Toxic Substance and Disease Registry, (ATSDR) copper can enter the environment through releases from the mining of copper and other metals, and from factories that make or use copper metal or copper compounds. Copper can also enter the environment through waste dumps, domestic waste water, combustion of fossil fuels and wastes, wood production, phosphate fertilizer production, and natural sources. Thus, copper is widespread in the environment. According to ATSDR, around 1,400,000,000 pounds which is 640,000,000,000 grams of copper were released into the environment by industries in 2000. In addition, copper is often found near mines, smelters, industrial settings, landfills, and waste disposal sites.

2.1.1.1 Used of Copper

There are many industrial uses of copper, due to its high ductility, malleability, thermal conductivity and resistance to corrosion. According to ATSDR, copper in liquid form is used as a wood preservative. It helps in restoration of original structures that are damaged due to dry rot. It is the main component of coins for many countries. Besides, about 65% of copper that is produced is used for electrical applications. The important uses of copper include, use in power generation and transmission of electricity. It is used in transformers, motors, bush bars, generators, and etc., to provide electricity throughout the country, safely and efficiently. In case of electrical equipments, copper is used in wiring and contacts for PC, TV, mobile phones and in the circuitry.

2.1.1.2 Health Affect of Copper

From ASTDR, copper is essential for good health. Nevertheless, when copper is exposure to higher dose it can be harmful. Long-term exposure to copper dust can irritate nose, mouth, and eyes, and also can cause headaches, dizziness, nausea, and diarrhea. In addition, when drink water that contains higher than normal levels of copper, it can cause nausea, vomiting, stomach cramps, or diarrhea. Purposely high intakes of copper can cause liver and kidney damage and even death. The Environmental Protection Agency (EPA) does not classify copper as a human carcinogen because there are no adequate human or animal cancer studies.

2.2 Current Technology for Removal of Heavy Metal

2.2.1 Precipitation

Precipitation is a process of addition of coagulants such as lime, iron salts, alum, and other organic polymers (Ahalya *et al.*, 2003). Precipitation process is the most familiar method for removing heavy metals up to parts per million (ppm) levels from water (Ahluwalia *et al.*, 2007). Precipitation is a simple and cost effective method for removal heavy metal. However, it is will produces large amount of sludge containing toxic compounds (Ahalya *et al.*, 2003). Besides, its efficiency is affected by low pH and the presence of other salts (ions). These precipitation method also requires an addition of others chemicals, which finally leads to the generation of a high water content sludge, which the disposal is cost intensive (Gray, 1999). Furtheremore, the precipitation with lime, bisulphide or iron exchange is lacks on the specifity and ineffective in the removal of heavy metal ions at low concentartion (Ahluwalia *et al.*, 2007).

2.2.2 Electro-coagulation

Electro-coagulation is an electrochemical approach, where in this process an electrical current was used to remove the metals from the wastewater (Ahluwalia *et al.*, 2007). Besides removing heavy metals, electro-coagulation is also an effective method in removing suspended solids, dissolved metals, tannins and dyes. The contaminants that presents in the wastewater are sustain in the solution by the electrica charges. When these ions and other charged particles are neutrilized with ions of opposite electrical charges provided by electrocoagulation system, they become destabilized and precipitate in a stable form.

2.2.3 Reverse Osmosis and Electro-dialysis

Reverse osmosis is a process in which heavy metals are remove by a semi-permeable membrane at a pressure greather than the osmotic presure caused by the dissolved solids in wastewater (Ahalya *et al.*, 2003). Meanwhile, electro-dialysis is a process which the heavy metals are remove through the use of semipermeable ion-selective membranes (Ahalya *et al.*, 2003). An electrical potential and the two elctrodes will causes a migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes it will cause the cells of concentrated and dilute salts are formed. For this reverse osmosis and electro-dialysis, both method requires the use of semi-permeable membranes for the removal of heavy metal ions from wastewater. Both methods give disadvantages for the removal of heavy metal. Which for reverse osmosis, it is an expensive method and for electro-dialysis the disadvantages is the formation of metal hydroxides, which clog the membrane.

2.2.4 Cementation

Cementation is another type of precipitation method implying an electrochemical mechanism in which a metal will having a higher oxidation potential passes into the solution (Ahluwalia *et al.*, 2007). For example, the oxidation of metallis ion, Fe (0) to ferrous iron (II) to replace a metal having a lower oxidation potential. Copper is the most commonl separated by cementation along with noble metals such as Ag, Pb and Au as well as As, Pb, Sb and Sn can be remove in this manner.

2.2.5 Electro-winning

Electro-wining is an extensively used in the mining and metallurgical industrial operations for heap leaching and acid mine drainage. Besides, it is also used in the metal transformation and electronics and electrical industries for removal of heavy metals (Ahluwalia *et al.*, 2007). Metals like Au, Cd, Cr, Ag and Zn present in the effluents can be recovered by electro-deposition using insoluble anodes (Gray, 1999).

2.3 Adsorption

According to Geankoplis (2003), adsorption processes is one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished. Usually, in commercial processes, the adsorbent is on the form of small particles in a fixed bed. The fluid will passed through the bed and the solid particles will adsorb components from the fluid. When the bed is about to saturated, the flow in this bed is stopped and the bed is regenerated thermally. The adsorbed material is thus recovered and the solid adsorbent is ready for another cycle of adsorption.

Adsorption is commonly preferred for removal of heavy metal ions due to its high efficiency, easy handling, availability of various adsorbents and cost effectiveness (Reed *et al.*, 1997). Besides, adsorption also gives advantages of less capital investment and land, simple design rules and operation (Markovska *et al.*, 2006). In addition, adsorption process can remove both organic and inorganic constituents even at very low concentration, it is relatively easy and safe to operate, both batch and continuous equipment can be used, no sludge formation and the adsorbent can be regenerated (Mohanty *et al.*, 2005). Furthermore, adsorption is economical because it is requires low capital cost.

2.4 Adsorption Isotherm

2.4.1 Freundlich Isotherm

The Freundlich isotherm Equation (2.1), which is empirical, often approximates data for many physical adsorption systems and is particularly useful for liquids:

$$q = Kc^n \tag{2.1}$$

where K and n are constant and must be determine experimentally. If log-log plot is made for q versus c, the slope is the dimensionless exponent n. The dimensions of K depend on the value of n. The linear form of this equation is given as Equation (2.2):

$$\log q = \log K + n \log c \tag{2.2}$$

2.4.2 Langmuir Isotherm

The Langmuir isotherm has a theoretical basis and is given as (2.3):

$$q = \frac{q_o c}{K + c} \tag{2.3}$$

where q_o and K is constant. q_o is kg adsorbate/kg solid and K is kg/m^3. The equation was derived assuming that there is only a fixed number of active sites available for adsorption, that only monolayer is formed, and that the adsorption is reversible and reaches an equilibrium condition. The linear form of this equation is given as (2.4):

$$\frac{1}{q} = \frac{K}{q_o c} + \frac{1}{q_o} \tag{2.4}$$

2.5 Adsorbents for Removal Heavy Metal

An adsorbent is a substance that is generally porous in nature and with a high surface area that can adsorb substances onto its surface by intermolecular forces. There are various types of adsorbent that has been studied for the removal of heavy metal.

2.5.1 Diethylenetriamine-grafted Poly (glycidyl methacrylate) (PGMA-DETA)

From Lui *et al.*, (2006), PGMA-DETA adsorbent achieved excellent adsorption performance in copper ion removal and the adsorption was most efficient